LIMITING OPALESCENCE TEMPERATURE IN SODIUM SILICATE GLASSES

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The calculation of the limiting opalescence temperature is proposed based on a model describing the mechanism of the formation of internal stresses in glass in cooling. The notion of the range of increased mobility of structural elements is introduced, which is identified with the glass softening range.

The notion of the "liquation cupola" as the dependence of the limiting immiscibility temperature on the composition is used to describe the state of the immiscibility of components in the melt and later in the solid phase. Since the moment of the transition of a system from the state of "turbidity" to the state of clarity can be visualized in glasses, the temperature of this transition is taken as the limiting temperature. It is assumed to be obvious that glass compositions corresponding to the isothermic bounds of the cupola correlate with the phases in which the solution disintegrates. In other words, with a varying temperature the composition of the immiscible phases keep constantly changing, in particular, at the upper point of the "cupola" they coincide, and starting with this temperature the structure become homogeneous regardless of its composition.

At the same time, it is evident that the fact of the disappearance of opalescence does not yet prove the homogenization of the structure, but points to the fact that there is no longer a defined interphase boundary, in particular, that this boundary becomes blurred, while heterogeneity areas may persist. For heterogeneity to be revealed in clear glass capable of liquation, which is a fact little doubted by contemporary researchers, such glass has to be heat-treated, which results in the formation of opalescence.

The existence of heterogeneities beyond the cupola bounds up to a temperature around 1400°C is recognized by many authors, but only as thermal fluctuations. This is corroborated, for instance, by the results of studying the temperature-concentration dependences of electromotive force (EMF) in sodium silicate melts [1]. Furthermore, the authors in [1] regard their data "as an indication of an obvious tendency for the formation of isolated stoichiometric groups in low-alkali sodium silicate melts". For instance, the "EMF – composition" isotherm at a temperature of 800°C in the

range of the molar contents of Na_2O below 20% is virtually parallel to the "composition" axis, i.e., the EMF does not depend on the composition of glasses investigated. Hence it follows that "different initial melts disintegrate into phases with identical compositions". Furthermore, according to EMF measurement data, variations in temperature – from clarification to intense opalescence – result in a shift of the matrix phase composition less than by 1%, i.e., a perceptible change in the structure does not change the composition. An indirect corroboration of this fact is good agreement of experimental data with analytical expressions describing the dependence of various properties of liquating glasses on the composition, which were obtained based on the same assumptions [2 – 4].

Thus, the curve called the "liquation cupola" cannot be regarded as the line of equilibrium between the phases. This is mapping of the dependence of the limiting opalescence temperature on the composition, whereas earlier presented model concepts [4] make it possible to obtain its analytical expression.

The formation of heterogeneities, which under appropriate conditions act as a basis for liquation, is hardly a result of thermal fluctuations, which in particular the authors in [1] suggest. These heterogeneities are related to the specifics of the interaction between the structural elements, where the tendency for merging of homogeneous structural elements prevails over the possibility of a uniform distribution of heterogeneous elements over the volume. The thermal motion erodes the heterogeneities bounds and the more so, the higher the temperature. Under rapid cooling (hardening) the liquid state structure persists in solid glass as well, including the blurred bounds of the heterogeneous areas. This accounts for an apparent optical homogeneity of glasses whose compositions are within the liquation range. The discrepancy between the structure and the temperature of the system generates inner stresses, this, accordingly, produces additional

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energy, i.e., the deformation energy concentrated near the boundaries of the heterogeneous areas.

The reason for such discrepancy is a low mobility of structural elements, which interferes with the processes of establishing an equilibrium state. Under thermal treatment (annealing) due to an increasing mobility of structural elements a part of deformation energy is transformed into the surface energy of the separated phases: a clearly defined boundary is formed and opalescence emerges; each level of residual stress energy in equilibrium conditions corresponds to a certain level of thermal energy of structural elements, namely, the part of energy that is related to their mobility. As the temperature grows, the residual stresses decrease and the thermal energy increases, and when an equilibrium is established between them and then shifts in favor of thermal energy, the interphase boundaries become eroded and the opalescence disappears.

In order to determine the limiting temperature of the existence of opalescence, one should find the dependence between the mechanical stress energy, which becomes transformed into the surface energy of the interphase boundary, and the thermal energy of the boundary layer facilitating the erosion of the boundaries.

Let us determine the mechanical stress energy. Let us consider the energy of interaction between the structural elements of a two-phase system or, more precisely, the average volume density E of this energy. Let the phases be integrated by structural elements A (SiO_2) and B ($Na_2O \cdot 4SiO_2$). Then

$$\begin{aligned} E &= E_A\, w_A + E_B\, w_B\,; \\ w_A + w_B &= 1, \end{aligned} \qquad (1)$$

where E_A and E_B are the volume densities of the energy of the interaction between the structural elements of the respective phases ($A - A$ and $B - B$); w_A and w_B are the volume parts of the respective phases depending on the glass composition.

By transforming expression (1) into the form of Eq. (4) in [4]:

$$E = E_A\,(1-x) + E_B\,x + \frac{(E_B - E_A)(1-k)}{k(1-x)+x}\,x\,(1-x), \qquad (2)$$

where x is the molar content of the structural element B in the glass of the composition $xB\,(1-x)A$; $k = V_A/V_B$ is the ratio of the molar volumes of the structural elements,
we obtain the desired energy value. This is the last summand responsible for the interaction between the structural elements A and B in the boundary interface region.

As was noted in [4], x may not coincide with the molar content of the chemical component giving the name to the system, since the structural element itself may be a certain chemical compound made up by initial components.

Obviously, the state of a system in which the interface between the zones with different values of the energy volume density is absent is non-equilibrium. The nonequilibrium is manifested in the inner stress arising in the zone of contact between the phases, and its energy is represented by the third summand in expression (2). In system with a sufficiently high mobility of structural elements this stress is the motive force in the formation of an phase boundary.

If the mobility of the structural elements is not sufficient, the stresses become "frozen". This usually occurs in fast cooling (hardening) of the melt. An exposure at an increased temperature (annealing) "revives" the structural elements and turns on the mechanism bringing the system closer to an equilibrium state. Thus, the probability of the formation of the phase boundary depends not only on the extent of supercooling of the system, but on the mobility of its structural elements as well.

Suppose the conditions have been created where the inner stress energy can be transformed into the interface energy. A temperature decrease increases the degree of overcooling and the stress energy, consequently, decreases the surface energy as well. This agrees with the fact that at lower temperatures the scattered phase exists (depending on its composition) in the form of a great number of drops of a relatively small diameter. A temperature rise decreases the surface energy and simultaneously decreases the number of drops of the scattered phase, at the same time increasing their average diameter. These consideration agree with the known experiments in small-angle scattering [5] which demonstrated that the mean radius of the scattered phase drops grows linearly with increasing temperature.

Let us take the equality of the inner stress energy and the thermal energy related to the mobility of structural elements in the boundary region as the condition determining the limiting temperature of the existence of an interphase surface:

$$(E_A - E_B)\,x\,(1-x)\,\ln k = \Delta H; \qquad (3)$$

$$\begin{aligned} \Delta H &= c\theta; \\ \theta &= t_b - t_m, \end{aligned} \qquad (4)$$

where ΔH is the variation in the enthalpy of structural elements in heating starting with the first manifestation of the mobility of structural elements t_m to the limiting temperature of the existence of opalescence t_b; c is the part of the heat capacity of a volume unit related to the relative migration of heterogeneous structural elements.

Equation (3) uses the result of averaging the part of expression (2) depending on k by x (see formula (5) in [4]):

$$\int_0^1 \frac{1-k}{k(1-x)+x}\,dx = -\ln k.$$

As the right-hand part of Eq. (3) is positive, at $k > 1$ the difference $E_B - E_A$ has to be negative.

In Eq. (3) one should take into account the variation in k with increasing temperature due to an increasing molar volume of the structural element B (the temperature expansion
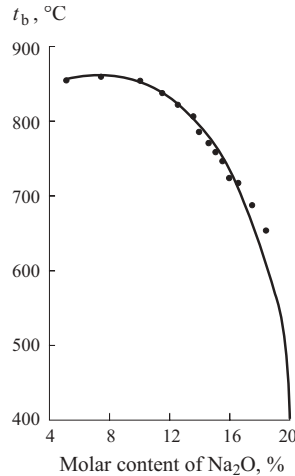
Fig. 1. Estimated dependence of the limiting opalescence temperature on glass compositions in $Na_2O - SiO_2$ system. Experimental dots based on the data from [7]; $u = 3.38 \times 10^4$ K; $\beta_1 = 2.7 \times 10^{-5}$ K^{-1}, $\beta_2 = 5.5 \times 10^{-5}$ K^{-1} from data by V. E. S. Turner [6].

Fig. 2. Dependence of vitrification temperature and minimal temperature of increased mobility of structural elements in glasses of $Na_2O - SiO_2$ system on their compositions [6]. Based on the data by: ●) V. E. S. Turner; +) M. O. Samsohen; ×) A. Ditzel and H. A. Sheibani; ⊙) V. Seddon and V. E. S. Turner; ◇) B. K. Schmid, A. N. Finn, and G. K. Young; ——) t_m.

of structural elements A can be neglected). It is simple to show that

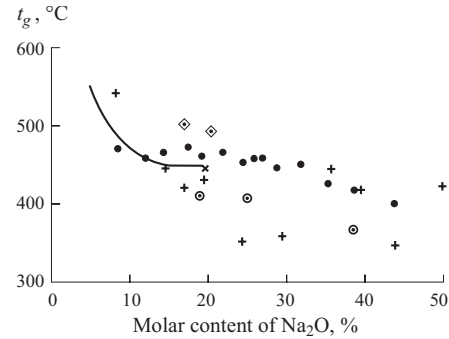$$\ln k = \ln k_0 - \beta_1 \theta_1 - \theta(\beta_2 - \beta_1), \qquad (5)$$

where k_0 is the value of k at room temperature t_0 (for sodium silicate glass $k_0 = 1.08$); β_1 and β_2 are the values of the temperature coefficients of the volume expansion of the structural elements B within the temperature ranges (t_0, t_m) and (t_m, t_b), respectively; $\theta_1 = t_b - t_0$.

The values of the coefficients β_1 and β_2 are obtained from TCLE data supplied by Turner [6] converting α to the volume coefficient: $\beta = 3\alpha$. For each site the variation in β with increasing temperature was neglected. Assuming that in the interval (t_m, t_b) the values E_A and E_B do not change, it follows from Eqs. (3) and (4) that for all compositions in the interval of x varying from 0 to 1 the value

$$u = \frac{\theta}{x(1-x)\ln k} \qquad (6)$$

has to remain constant. The values $\theta(x)$ were determined based on the data from [7] for the dependence of the minimal clarification temperatures t_b on the alkali oxide content. The minimal temperature of increased mobility of structural elements t_m for most compositions was taken equal to 450°C, and all glasses were annealed at this temperature for 10 h before thermal treatment [7]. The specified temperature, according to the data in [6], is close to the vitrification temperature.

The vitrification temperature t_g is related to the softening state [8] and is determined by dilatometric measurements based on a perceptible increase in the TCLE. It depends not only on the composition, but on other factors as well, in par-

ticular, on the heating or cooling rate. In any case the spread in t_g values given by different authors [6] may constitute tens of degrees, however, a tendency of the vitrification temperature increasing, as the compositions approach pure silica, is generally observed. Therefore, identifying the increased mobility temperature as the vitrification temperature appears quite justified.

Based on the condition of the constancy of the value u, its value was determined which provided for the optimum description of the experimental dependence by the estimated dependence $t_b^{th} - x$ within the range of insignificant variations of t_m with varying compositions. Next, using Eqs. (6) and (5) for the preset value of u, the values of θ were determined:

$$\theta = \frac{ux(1-x)(\ln k_0 - \theta_1 \beta_1)}{1 + ux(1-x)(\beta_2 - \beta_1)}, \qquad (7)$$

and using expression (7) the theoretical values of t_b^{th} were determined for the compositions with the molar content of the alkali oxide below 13%:

$$t_m^{th} = t_b^{exp} - \theta.$$

The t_b^{th} values were experimental values from [7]. In the composition range with the molar content of the alkali oxide over 13% the values t_b^{exp} were calculated:

$$t_b^{th} = t_m^{exp} + \theta.$$

The result of the correlation of the values t_b^{th} calculated in this way with the experimental data is shown in Fig. 1, with $t_m^{exp} = 450$°C in the specified range. The same figure gives the values of the parameter u and the values β_1 and β_2 [6] used in the calculation. It can be stated that the structural

model of liquating alkali-silicate glasses proposed in [2] for the room temperature range adequately describes the state of glasses within the opalescence temperature interval as well.

Figure 2 shows data supplied by different authors [6] on vitrification temperatures (dots) and the function t_m used in the calculations (the curve). It can be seen that the curve of t_m variation depending on the composition is within the range of known experimental vitrification temperatures and follows the general tendency of increasing as the compositions approach that of pure silica.

Thus, vitrification temperatures determine the beginning of the range of increased mobility of structural elements, where the processes directed to restoring the equilibrium between the structure and the temperature are switched on. The disappearance of opalescence in this case is related not to the homogenization of the structure caused by leveling of the compositions of the coexisting phases, but is due to the erosion of the boundary between the heterogeneity zones, while their compositions remain unchanged.

The method proposed makes it possible to calculate the inner stress energy in liquating glasses, if the values of the energy of the interaction between homogeneous structural elements are known.

REFERENCES

1. A. F. Borisov and V. I. Solov'ev, "A study of liquation processes in a sodium silicate system using the electromotive force method," in: *Liquation Phenomena in Glasses, Proc. 1st All-Union Symposium* [in Russian], Nauka, Leningrad (1969), pp. 54 – 58.
2. V. V. Samoteikin and O. A. Gladushko, "Account of structural specifics in the model of conductance and diffusion in liquating alkali-silicate glasses," *Steklo Keram.*, No. 5, 15 – 18 (2002).
3. V. V. Samoteikin and O. A. Gladushko, "Interaction between ingredients of two-component silicate glasses," *Steklo Keram.*, No. 5, 17 – 20 (2003).
4. V. V. Samoteikin, "Interaction between structural elements in two-component glasses," *Steklo Keram.*, No. 4, 15 – 17 (2004).
5. D. A. Goganov and E. A. Porai-Koshits, "Modification of the supermolecular structure of sodium silicate glass in heating," Dokl. Akad. Nauk SSSR, **165**(5), 155 – 160 (1965).
6. O. A. Mazurin, M. V. Strel'tsina, and T. P. Shvaiko-Shvaikovskaya, *Properties of Glasses and Glass-Forming Melts. Reference Book, Vols. 1 and 4* [in Russian], Nauka, Leningrad (1973, 1980).
7. N. S. Andreev, D. A. Goganov, E. A. Porai-Koshits, and Yu. G. Sokolov, in: *Vitreous state. Issue 1. Catalyzed Crystallization of Glass* [in Russian], Izd-vo Akad. Nauk SSSR, Moscow – Leningrad (1963), pp. 46 – 53.
8. A. A. Appen, *Chemistry of Glass* [in Russian], Khimiya, Leningrad (1970).